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PREPARATION AND PROPERTIES OF THIN FILM $Ga_x In_{(1-x)}$ AND $GaAs_x Sb_{(1-x)}$ ALLOY FILMS

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Epitaxial alloy films were grown from solutions using three versions of the growth reactor. An effort was made to closely monitor the reducing quality of the H_2 atmosphere in the reactor. Failure to grow suitably thin films is attributed to the inadequate quality of this atmosphere.

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INTRODUCTION

This report describes the attempts to grow GaAs-InAs and GaAs-GaSb alloy films on GaAs substrates with and without an intermediate alloy layer. Emphasis was to be placed on thin smooth films. An absolute preliminary goal for success would be the ability to grow smooth thin GaAs films on GaAs. We had previously demonstrated that we could grow adequate single layers by vertical dipping and had explored its use for alloy growth. The goal of multiple layers precluded the vertical dipping approach and suggested a horizontal slider system with multiple melts. We pursued this unsuccessfully in the growth of thin GaAs films and were doomed to failure with the alloy films with respect to thickness and smoothness. The following is a description of the attempts to eliminate what we believe to be the prime cause of failure, the presence of excessive H_2O in the H_2 carrier gas. Our attempts to solve this problem are described below. Areas which we believe will be useful for future work by others include the use of calcia stabilized zirconia as electrolytic gauges and pumps for monitoring and reducing the H_2O concentrations in H_2. Others are the use of anodic oxidation to etch alloy films precisely and to provide high densities of Ga droplets on substrates as nucleation centers.

GaAs SUBSTRATES

Gallium arsenide substrate wafers used in this work were from boat grown crystals. Three sources of these boat grown crystals were used. The initial work was based on crystals from Crystal Specialties and ones grown in our laboratories. The former had a larger cross sectional area and both had comparable dislocation densities, $\sim 5000 \text{ cm}^{-2}$. The third source from Laser Diodes had dislocation densities in the $100\text{-}200 \text{ cm}^{-2}$ range and were supplied as wafers which had a surface corresponding to lapping with 3200 grit. Other wafers were sawed from the bulk crystals using silicon carbide blades and then lapped with 3200 SiC grit. Wafer orientations of (211), (311), (100) and (111) were established to within 0.5° using a laser beam optical goniometer and the (110) cleavage planes of GaAs. This instrument was developed in our laboratories and has an inherent precision of $\pm 0.1^{\circ}$ except for kerf loss irregularities which account for the majority of the 0.5° uncertainty.

After lapping on both sides, the wafers were chemically polished to remove at least 75 μm so as to minimize the possibility of residual surface damage from the prior sowing and lapping steps. The chemical polishing was done on either Politex Pix or Supreme polishing pads from Geoscience. These have a self adhesive back and were mounted on a 12" diameter glass disc rotating at 40 rpm. The substrates were supported on a freely rotating eccentric fixture with a diameter of 4". An alkaline polishing solution was used. This was prepared from Mirrolite Polishing Compound supplied by the Materials Development Corporation. Early

batches of this etchant gave good surfaces but recent ones left scratches. The overall experience with Mirrorlite is that it is substantially less reliable than the methanol-bromine solutions used earlier. The latter requires much better ventilation and this was the reason we made the change. Quality control in the Mirrolite multiphase system will always be a more serious problem than for etchants consisting of a single phase.

Another variable in preparing substrate surfaces is associated with removing the last vestiges of wax used to cement the wafers to the chemical polishing fixture. Apiezon W Wax was used because of its relative resistance to attack by the aqueous alkaline oxidizing polishing medium. Great care is suggested in not overheating the wax least the difficulties in removing all of it be insurmountable. Toluene is preferred over trichloroethylene as a solvent. The wafers are washed with warm tuluene in a soxlet extractor using approximately 60 cycles. After this cleaning step wafers were stored in plastic envelopes until a final etch immediately before loading in the epitaxy reactor.

The final etch was made in 5:1:1 conc H_2SO_4, containing equal volumes of water and 30% H_2O_2. This etch was prechilled to about 5°C before adding the H_2O_2. Addition of the H_2O_2 raised the temperature to near room temperature. Before etching the substrate wafer in the 5:1:1, the wafer was wet with a solution containing by volume 7 parts conc H_2SO_4 and one part H_2O. The heat of mixing of these two solutions are small so that no temperature rise during the etching was experienced. Similarly, the 7:1 solution was used as a first rinse after the final 30-90 sec etch in

the 5:1:1. This was followed by rinses with a solution containing 3 parts by volume conc H_2SO_4 and 1 part H_2O and lastly, rinses with D.I. water. The acid and water rinses leave the GaAs surfaces hydrophobic which are blown dry with a nitrogen stream. This clean-up etch always is detrimental to the quality of the surface polish because it is selective. We had intended to pursue alternate final surface cleaning procedures such as anodic oxidation followed by acid stripping. As will be discussed below, this final etch problem was of much less gravity than vapor phase etching in the epitaxial reactor.

UNCONTROLLED VAPOR PHASE ETCHING OF THE SUBSTRATES

Dr. Li in these laboratories had established the minimum conditions necessary for growing a thin GaAs epitaxial film on a GaAs seed, namely the preservation of the smooth substrate surface.[1] The same conditions apply to the growth of thin epitaxial films of Ga, InAs and GaAs, Sb alloys. There are two prime mechanisms for degradation of the substrate surfaces prior to epi growth. One is always dominant. These will be discussed separately but not necessarily in the frequency with which they occur.

Hydrogen is the most commonly used carrier gas in both liquid and vapor epitaxial systems because of its relatively large reduction potential and because it is moderately convenient to purify. For the first case of pregrowth substrate errosion we will assume the carrier gas is pure H_2. As the substrate warms and reaches the growth temperature in the pregrowth period, the equilibrium vapor pressure of both Ga and As increase

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with that of As being higher. This leads to local melting on the substrate at those regions which have higher unit surface free energies such as those about dislocations which intercept the surface. Once a local region begins to melt, i.e., to form a saturated liquid solution of Ga and As, that region tends to grow in size because the loss rate of As from the solution is much higher than from a solid GaAs surface. This loss is replenished by further melting to keep the solution saturated. Pitting is the overall result. Addition of As to the H_2 carrier gas is the basic remedy. This might be done by maintaining one source at an appropriate temperature downstream or by adding AsH_3 to the H_2 which decomposes at the growth temperature to As gas and H_2. A more convenient approach for GaAs is to maintain a downstream GaAs source at or above the growth temperature so as to provide nearly equilibrium gas composition over the substrate. The necessity of adding arsenic to the carrier H_2 increases as the growth temperature increases because of the higher equilibrium pressure of the As and its associated faster loss rate if not otherwise supplied. Local melting is not as readily detectable and thus not as serious for substrates with low index orientations such as (100) and (111). It is a major factor for substrates orientated in (311) and (211) directions and can in fact be used to delineate dislocations for the latter two orientations. As a compromise, one can protect the substrates from full exposure to the H_2 gas stream by arranging to have a cover plate over them prior to growth. This trades against the utilization of the H_2 to reduce the oxides on GaAs which should always be assumed to result from etching in aqueous

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oxidizing solutions and rinsing in water. This leads to the second mechanism for surface errosion prior to growth.

Oxide thicknesses on the substrates prior to loading in the reactor are most likely 20-50A thick and are reducible with relatively impure H_2 (containing no free O_2 and $\approx$ 50 ppm H_2O) below $750^\circ C$. The seriousness of H_2O being present in the H_2 is that it vapor etches the substrate. Failure to sufficiently limit the H_2O content in epitaxial reactors is the prime reason the successes of this project were so limited. Attempts to circumvent this difficulty lead to four types of reactors. The most positive results were the experience gained in how to reliably use calcia stabilized zirconia electrolytic pumps and guages for monitoring and reducing the water concentrations in H_2 streams. This will be described in detail in a later section. Returning to the prime problem of substrate vapor etching with surface errosion. The reaction of GaAs(s) with H_2O(g) in a flowing H_2 stream is favored at all reasonable growth temperatures in accord with the reaction: $GaAs(s) + \frac{1}{2}H_2O(g) \rightarrow \frac{1}{2}Ga_2O(g) + \frac{1}{2}H_2(g) + \frac{1}{4}As_4(g)$. Thermodynamically, this reaction proceeds essentially to completion and can in a pragmatic sense be stopped only by limiting the amount of available H_2O in the gas stream above the substrates. As an example if all the water vapor in a H_2 stream containing 10 ppm of H_2O and flowing at the rate of 400 ssc atm/min reacted with a GaAs substrate one cm^2 in area the average thickness erroded would be 10 μm in a typical pregrowth temperature equilibration period of 100 minutes. The conditions suggested are typical ones except for the assumption of total water vapor reaction:
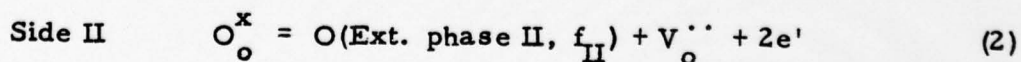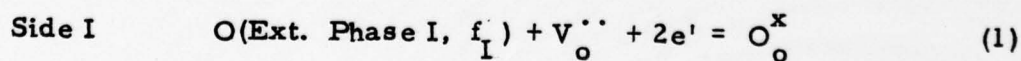
reducing this to only 10% reduces the average errosion to 1 μm. If this were uniform, the effect would be relatively unimportant if the etching were uniform. This is not the case, in part because the unit surface free energy over the substrate is not constant but varies for example, in the region near dislocations as compared to regions relatively far removed from a dislocation. The host of papers on vapor phase etching/epi growth illustrate the non-uniformities of the substrate surface. Gas flow patterns are additional factors. The vapor etching of our substrates lead to four major reactor modifications and testing of calcia stabilized zirconia tubes as solid electrolytes in guages for measuring oxygen fugacities in the H_2 gas stream and to electrolytically removing H_2O from the stream. A description of this is given below and followed by that of the reactor designs.

USE OF CALCIA STABILIZED ZIROCNIA AS GAUGES AND PUMPS FOR OXYGEN

Calcia stabilized zirconia impervious tubes are supplied by the Zirconium Corporation of America. This material has a substantial electrical conductivity due to mobile oxygen ions. It is a reasonable ionic conductor over a wide range of useful oxygen pressures, $\sim 10^{-40}$ to > 1 atm and within this range is a very poor electronic conductor at temperatures between 500-600 C. These are the characteristics needed for a gauge or pump. Substitution of 7.5 m/o of Ca^{++} ions for Zr^{++++} ions in calcia stabilized zirconia (CSZ) greatly increases the concentration of the compensating defect, oxygen ion vacancies. By doping with large

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amounts of CaO, the vacancy concentration is fixed for all intensive purposes irrespective of the oxygen pressure from a very small value to a very large one such that 7.5% of the oxygen sites are now vacant. The Ca defects on lattice sites nominally occupied by Zr ions are described by the symbol, Ca''_{Zr}. The two superscript dashes indicate two positive charges relative to the nominal charge of the site occupied by the subscript ion. Similarly an oxygen ion vacancy is described by the symbol, $V_O^{\cdot\cdot}$ where each single superscript dot indicates a relative positive charge. The symbol, O_o^x represents an oxygen ion on its proper site and the superscript x is a reminder that the species has a relative charge of zero. Holes and electrons as defects are represented respectively as $h^{\cdot}$ and e'. Consider the inner and outer surfaces of a CSZ tube as being side I and II respectively and the corresponding oxygen fugacities at the surfaces being fixed as f_I and f_{II} by being in equilibrium within an external phase, either gaseous or liquid solutions on the respective sides. If f_I is not equal to f_{II}, oxygen in the external phase where its fugacity is high tends to flow spontaneously from the surface where its fugacity is higher to the extended phase in which the fugacity is lower. This process can be described in terms of two half cell reactions: occuring under conditions where the sides are shorted so that transport of both electronic and ionic defects is possible.

$$\text{Side I} \qquad O(\text{Ext. Phase I, } f_I) + V_o^{\cdot\cdot} + 2e' = O_o^x \qquad (1)$$

$$\text{Side II} \qquad O_o^x = O(\text{Ext. phase II, } f_{II}) + V_o^{\cdot\cdot} + 2e' \qquad (2)$$

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These reactions can be summed with the understanding that the activities of O_o^x, and $V_o^{\cdot\cdot}$ are found by the doping and are the same on both sides. Also the activity of the electrons are fixed by the assumption of a conducting path. For these conditions the sum of $(1+2)$ is:

$$O(\text{Ext. phase I}, f_I) \rightarrow O(\text{Ext. Phase II}, f_{II}) \tag{3}$$
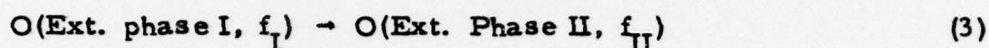
The change in Gibbs free energy for (3); ΔG_3 is $RT \ln f_{II}/f_I$ (R is the gas constant and T the thermodynamic temperature). If now reaction (3) is carried out under reversible conditions in an electrolytic cell the emf, E, is given by

$$\Delta G_3 = NFE , \tag{4}$$

where N is the equivalent of charge associated with reaction (3) which is 2 as seen by inspection of (1) and (2). Thus

$$E = \frac{RT}{2F} \ln \frac{f_I}{f_{II}} \tag{5a}$$

or

$$E = \frac{RT}{2F} \ln \frac{a_I}{a_{II}}$$

where a_I and a_{II} are the oxygen thermodynamic activities of surfaces I and II. Similar choices of standard states are presumed.

The measurement of E is relatively simple since the resistance of the cell is typically $\sim 10^4 - 10^5$ ohms. The electrical conductivity of the CSZ electrolyte is ionic so that internal shorting electronic current is

essentially nil except at sufficiently low values of the oxygen fugacity.

For cases in which the electric conductivity is not sufficiently small, a short circuit current flows within the cell such that the measured emf, Em, is related to the reversible emf, E, and the average fraction of the total electrical conductivity across the CSZ associated with electronic conductivity, $(te)_{ave}^{\sigma}$ is:

$$Em = E\left[1 - (te)_{ave} \right] \tag{6}$$

We have limited the use of CSZ gauges to the useful cases in which $(te)_{ave} \lesssim 0.005$ and can be essentially neglected. For pumps the value of te can safely rise to ~ 0.05. The limitations imposed on the gauges is at most a 1/2% error in E and will be neglected in the following and returned to later.

If the oxygen fugacity at surface I of the CSZ tube is established as that in equilibrium with H_2 and H_2O in an external gas phase, then one can write:
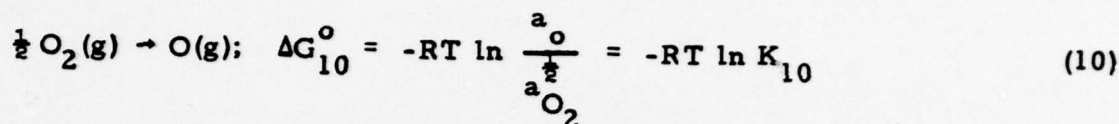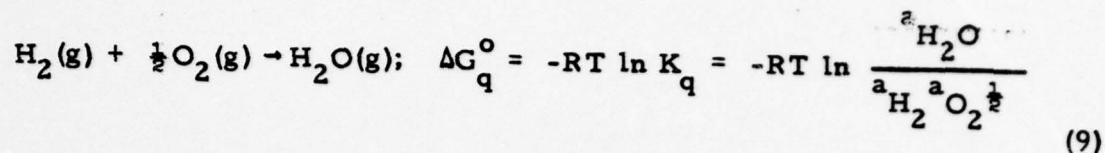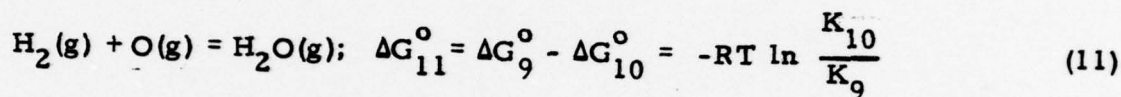
$$H_2(g, P_{H_2}) + O(a_I) \rightleftharpoons H_2O(g, P_{H_2O}) \tag{7}$$
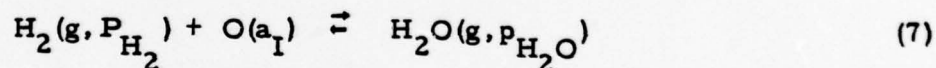
and

$$a_I = K_7 \left[\frac{P_{H_2O}}{P_{H_2}} \right]_I \tag{8}$$

where the subscript on the bracket refers to Side I. Standard states are chosen as the ones for gases at 1 atm in ideal gas states (standard state

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fugacity is 1 atm at 1 atm pressure) tabulated K_7 is available by combining the standard state free energies for reactions (9) and (10)

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g); \quad \Delta G_q^o = -RT \ln K_q = -RT \ln \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{\frac{1}{2}}} \tag{9}$$

$$\tfrac{1}{2}O_2(g) \rightarrow O(g); \quad \Delta G_{10}^o = -RT \ln \frac{a_o}{a_{O_2}^{\frac{1}{2}}} = -RT \ln K_{10} \tag{10}$$

On (9-10)

$$H_2(g) + O(g) = H_2O(g); \quad \Delta G_{11}^o = \Delta G_9^o - \Delta G_{10}^o = -RT \ln \frac{K_{10}}{K_9} \tag{11}$$

$$K_7 = K_{10}/K_9 \tag{12}$$

It will be furthermore assumed that the H_2O and H_2 can be approximated as ideal gases so that $a_{H_2O}/a_{H_2} = P_{H_2O}/P_{H_2}$. Fixing the activity of oxygen at surface II by equilibration with its external phase, and measuring E at a known T provides a means for obtaining $\left(P_{H_2O}/P_{H_2} \right)_I$. For example, if the reference side of the cell (Side II) is equilibrated with a hydrogen atmosphere saturated with water vapor at $0^{\circ}C$, a relatively easy reference mixture to reproduce, the ratio, $\left(P_{H_2O}/P_{H_2} \right)_I$, can be obtained from (5b) and (8), namely

$$E = \frac{RT}{2F} \ln \left\{ \left[P_{H_2O}/P_{H_2} \right]_I \Big/ \left[P_{H_2O}/P_{H_2} \right]_{II} \right\}. \tag{13}$$

Equation (13) has been most conveniently used to determine the ratio

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$\left(P_{H_2O}/P_{H_2} \right)$ in inlet and outlet hydrogen streams used for the epitaxial reactors and is suitable at $500°C$ for detecting water concentrations in otherwise pure H_2 down to ~ 1 part in 10^8.

The general considerations in selecting a suitable reference system to establish an oxygen activity, a_{II}, are considered below.

Many oxygen activity reference systems have been used. These include gas mixtures, such as CO/CO_2 in suitably controlled ratios, which establish a reference oxygen activity via a platinum electrical contact/catalyst on the CSZ surface. We have extensively used its variant, H_2O/H_2, because of the relative ease in establishing a reproducible mixture with a convenient composition ratio by saturation at $0°C$ for measuring ratios of P_{H_2O}/P_{H_2} in the range of 10^{-7} to 10^{-3}. These figures correspond to oxygen activities on the CSZ surface equal to molecular oxygen gas pressures of 10^{-42} to 10^{-34} atm respectively. In principle, air on pure oxygen would be a satisfactory reference electrode gas in the sense that the oxygen activity is easily fixed at 1 or 0.2. Disadvantages are the resultant large pressure oxygen pressure differences across the CSZ wall, which is a sintered fine grained "generally impervious" ceramic tube, i.e., $\sim 10^{-34} - 10^{-42}$ orders of magnitude. In addition, any uncertainty in temperature enhances the error in the absolute value of $\left(P_{H_2O}/P_{H_2} \right)_I$. Differentiation of 13, assuming no error in measuring E or an uncertainty in the reference oxygen activity, shows that the fractional error in $\left(P_{H_2O}/P_{H_2} \right)_I$ is $\dfrac{2FE}{RT}$ or E(volts)/0.087 times the fractured error in the absolute temperature at

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500°C. Finally, the problem of measuring E to within the reasonable stability limit of the cell, ~ 0.1 mv, is more convenient with simple instrumentation if the emf is relatively small. These three considerations, limits to imperviousness of the CSZ tubes, temperature and voltage uncertainties, all point to the desirability of using a reference oxygen activity which is reasonably close (such as to within 3 orders of magnitude) to that being measured. In addition, the short circuit electronic current of the cell is proportional to the cell voltage which is fixed by the differences between the measured and reference oxygen activities.

Solid reference sources such as Ni/NiO, have been used to fix the a_{II}. The basic characteristic of these is that they indeed do react rapidly enough with the atmosphere to fix a_{II} at the CSZ surface and that they have a sufficiently electrical conductivity and do not make rectifying contacts. The latter point is served by making the contact area large and the measuring currents small such that the voltage drop across the contact, ΔV, satisfies the condition that the energy of a unit charge, $q\Delta V$, be small compared to its thermal energy. This condition is readily met at 500°C. In the case of NiO, the oxide is also an electronic conductor which is an advantage. Its disadvantage is the high equivalent oxygen activity associated with the Ni/NiO equilibrium at 500°C. This can be expressed as an equivalent ratio $\left(P_{H_2O}/P_{H_2} \right)$ whose value at 500°C is corresponding to $\sim 200/1$. We have used two metal oxide electrodes, one of which is novel and has proved to be convenient. The first if Ga/Ga$_2$O$_3$ which at 500, 550 and 600°C has oxygen activities equivalent to $\left(P_{H_2O}/P_{H_2} \right)$ ratios

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1.85×10^{-5}, 4.86×10^{-5} and 1.14×10^{-4} respectively. Thus at 500°C, the reference corresponds to only 18.5 ppm of H_2O in H_2, an almost ideal fit for measuring practical moisture contents in epitaxial H_2 streams. The only procedural point that needs to be made in using this electrode system is that the Ga_2O_3 has a sufficient high electrical resistivity that it should be largely eliminated between the Ga and CSZ wall and allowed to only form a film on the top of the Ga. This can be achieved by heating the Ga in H_2 in situ to reduce the oxides or by decomposing them by electrolytic pumping, which will be described subsequently, followed by the addition of a ~ 0.01 to 0.1 scc of O_2 to form the capping oxide. This procedure leads to a stable reference cell.

An improvement over the above reference electrode is to replace the Ga by its approximate Ga-In eutectic composition containing 16.5 a/o, so as to reduce the mp from 29.8°C to below nominal room temperature. A mixture close to the eutectic one is less likely to fracture the CSZ tube if it should freeze. In_2O_3 is so much less stable than Ga_2O_3 that it can be ignored as a component in the Ga_2O_3. In the eutectic mixture at 500°C the activity coefficient of the Ga is 0.86. Its temperature coefficient is small enough to be ignored. The net effect is to raise the equivalent ratios of $\left(P_{H_2O}/P_{H_2}\right)$ at 500, 550 and 600°C by 10% above the values given above for pure Ga with Ga_2O_3.

The measuring electrode is a 10 mil Pt wire wrapped with several twisted turns around the lower end of the CSZ tube coated with several applications of pure Pt paint which is free of inorganic glass binders.

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This paint is first diluted $\sim 50:1$ with acetone. Enough applicators are made so that sheet resistance is $\gtrsim 1000$ ohm/square. Typical contact areas are $\sim 1 \ cm^2$. It is important that the Pt particles allow the gas being tested to equilibrate with the CSZ surface. Diameters of the Pt particles are approximately 1 μm. For a sufficient degree of self adherence, the Pt coated CSZ guage tube is fired at $800^{\circ}C$ in air before use. The CSZ gauge tubes are most commonly 1/4" OD, 3/32" wall, 18" long with a round end closure (flat bottom ones are more susceptible to cracks). These tubes with electrodes can be cemented into quartz tubes using epoxy cement for vacuum applications such as a Varian's Torr Seal. Several versions of the electrolytic gauges and pumps were built. A very convenient pump modification is shown in Figure 1. It differs from the gauge in that the length of the inner and outer Pt electrodes are ~ 1 cm. These electrodes are prepared by painting on several coats of unfluxed Pt metal paint which had been literally diluted with acetone and firing in air to $800^{\circ}C$ for several hours. The reference electrode in this cell is equilibrated with H_2 saturated with water vapor at $0^{\circ}C$. The H_2O saturator, shown as part of the overall gas supply in Figure 2, is one in which the reference H_2 stream flows over a water reflux reservoir at $\sim 35^{\circ}C$, through a condensor cooled at a few degrees below room temperature and then through a column packed with glass beads and cooled with ice water. One objective was to avoid small pressure variations associated with H_2 bubbling through a column of H_2O. These were readily detectable. H_2 flow rates through the bubbler were between 10 and 50 scc/min. The
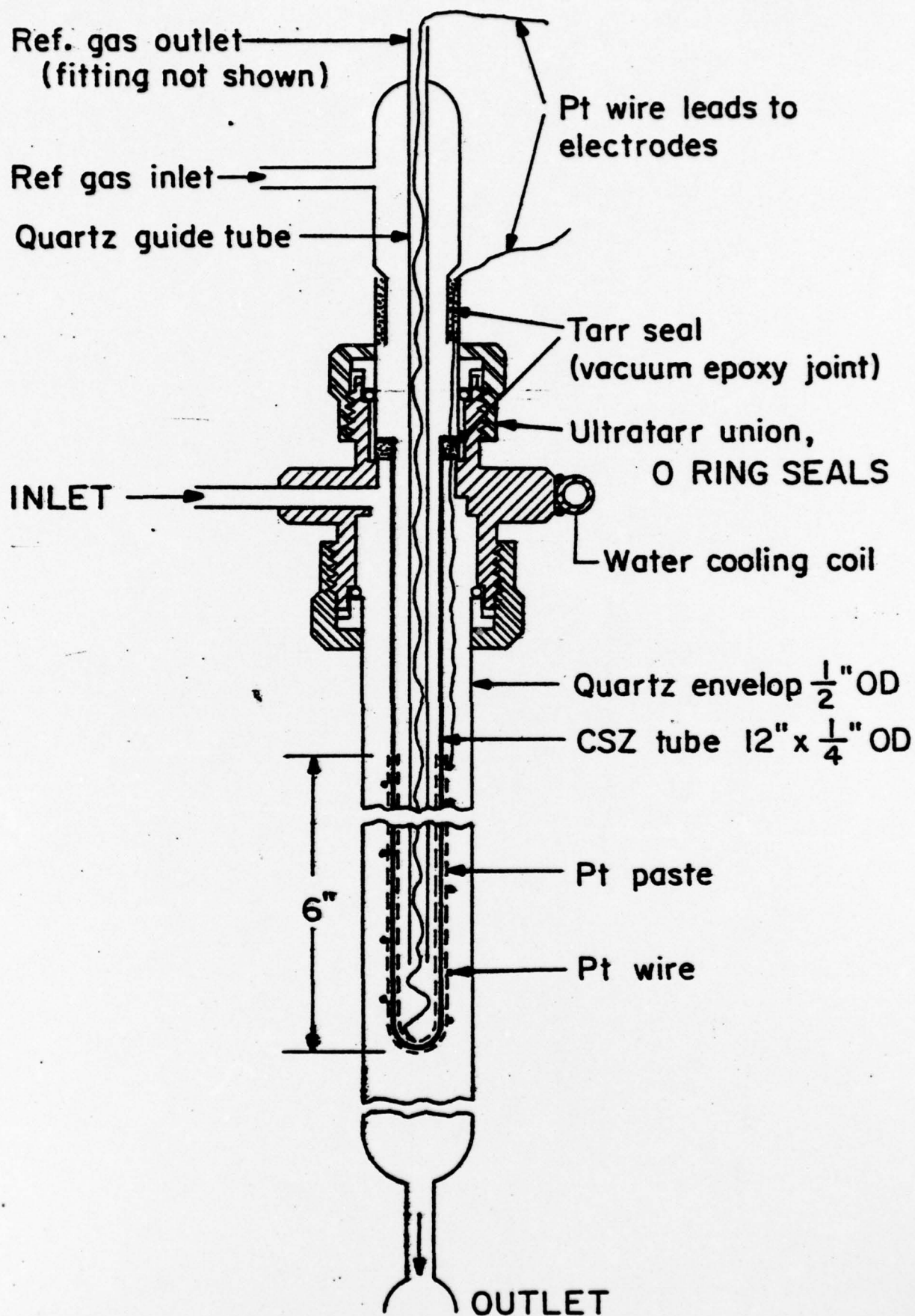
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Ref. gas outlet
(fitting not shown)

Pt wire leads to
electrodes

Ref gas inlet

Quartz guide tube

Tarr seal
(vacuum epoxy joint)

Ultratarr union,
O RING SEALS

INLET

Water cooling coil

Quartz envelop $\frac{1}{2}$"OD

CSZ tube 12"x $\frac{1}{4}$"OD

6"

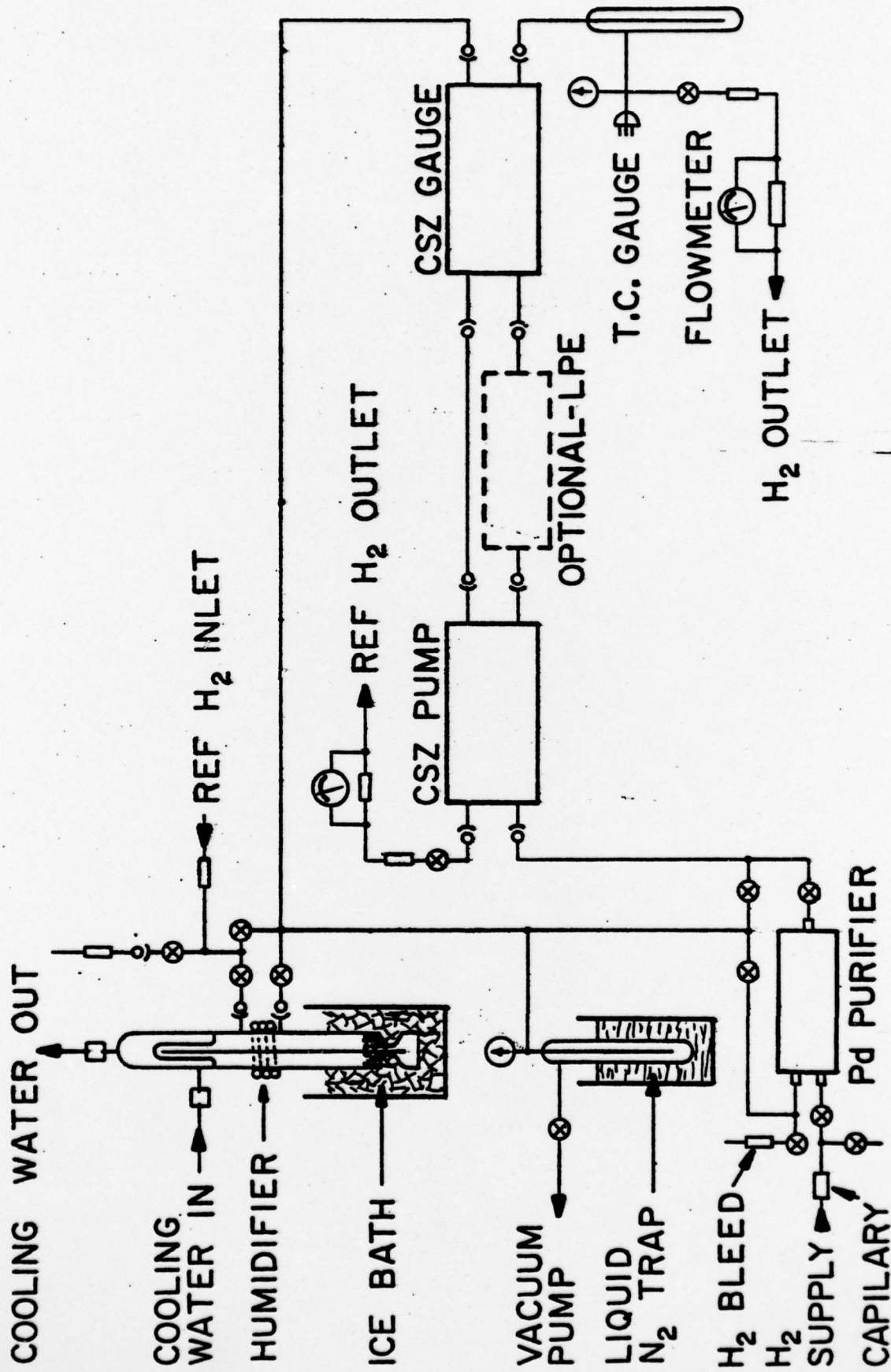Pt paste

Pt wire

OUTLET

Fig. 1. PUMP ASSEMBLY

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Fig. 2. Gas Flow Diagram for Purifying and Monitoring
H_2O Content in the H_2 Stream Used for Liquid
Phase Epitaxial Growth

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degree of saturation was independent of flow rate within this range. This reference gas was identical to one prepared by passing pre-chilled H_2 gas through a water bubbler at $0^\circ C$ in which the bubble diameter was limited to $\widetilde{<} 1$ mm.

Basic features of the H_2 gas system shown in Figure 2 were a CSZ pump and gauge on the respective inlet and outlet of the epitaxial reactor. Valves were glass O-ring type stopcocks. Connecting joints were polished ball and socket with O-rings. The flow meters which have a useful range from ~ 0.1 to 1000 scc/min. are all stainless steel with a minimum of fittings are based on an earlier USC design (U.S. Patent) Supply H_2 was first purified by diffusion through a Pd diffuser. For testing the gas system, the CSZ pump was directly connected to the CSZ gauge and the system operated at a slight positive pressure. As a preliminary check the H_2O/H_2 ratio determined from the gauge emf was found to vary in the expected manner with the pump current biased to add H_2O to the H_2. The results are shown in Figure 3. The linear variation and agreements between the expected and observed slopes indicated the reliability of the reference gas supply and that the Pt electrodes are adequately acting as catalysts to establish equilibrium between H_2O, H_2 and the CSZ surface of the gauge.

Typical ratios of H_2O/H_2 in the H_2 stream at the gauge as supplied by the Pd diffuser via the gas system were typically 2×10^{-6} for H_2 flow rates of ~ 100 scc/min. That this can be lowered as shown in Fig. 4 by an order of magnitude by biasing the CSZ pump to remove H_2O may have several
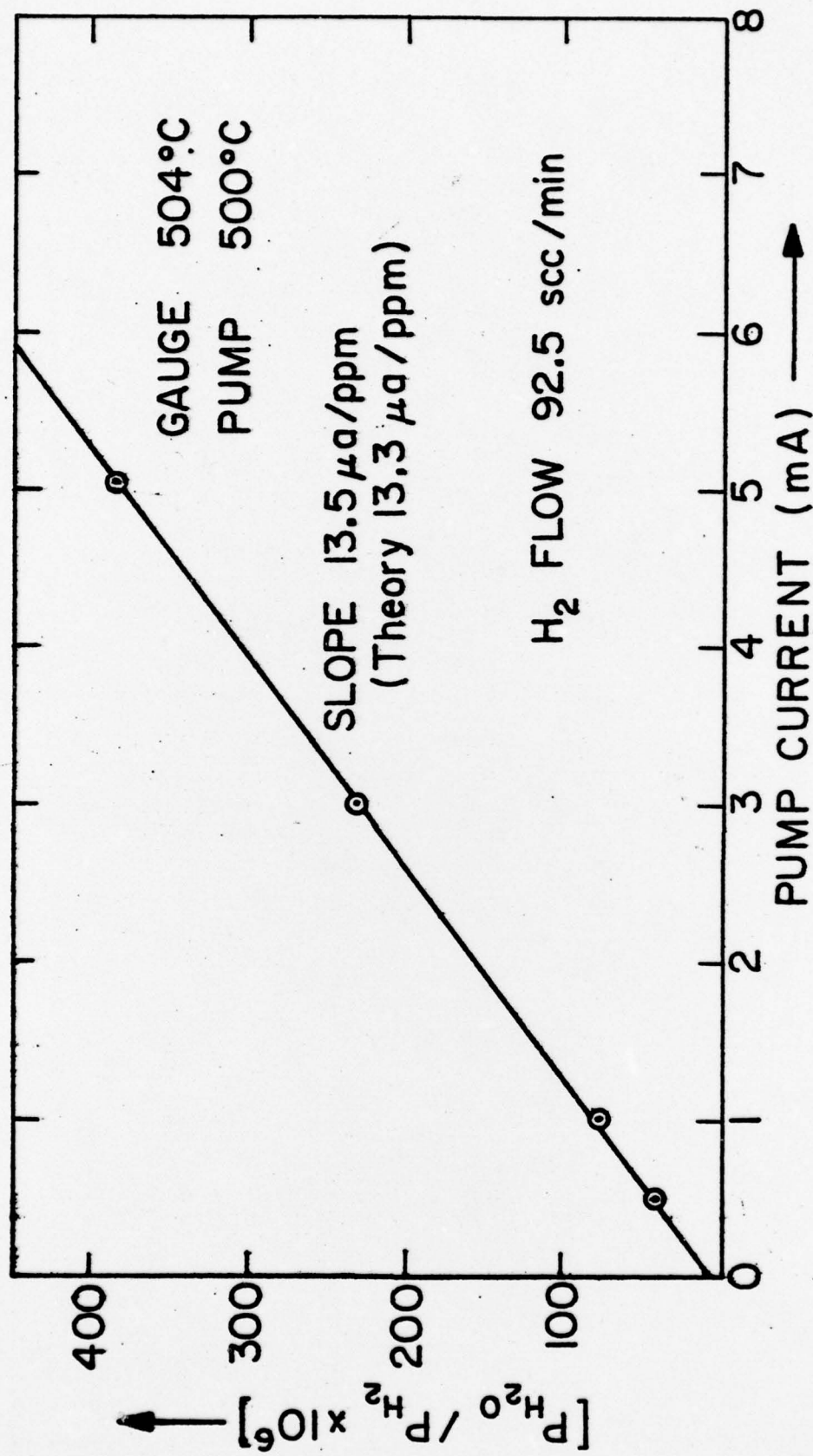
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Fig. 3. Variation of P_{H_2O}/P_{H_2} on Pump Current

GAUGE 504°C
PUMP 500°C

SLOPE 13.5 μa/ppm
(Theory 13.3 μa/ppm)

H_2 FLOW 92.5 scc/min

PUMP CURRENT (mA)

$[P_{H_2O}/P_{H_2} \times 10^6]$

-16a-
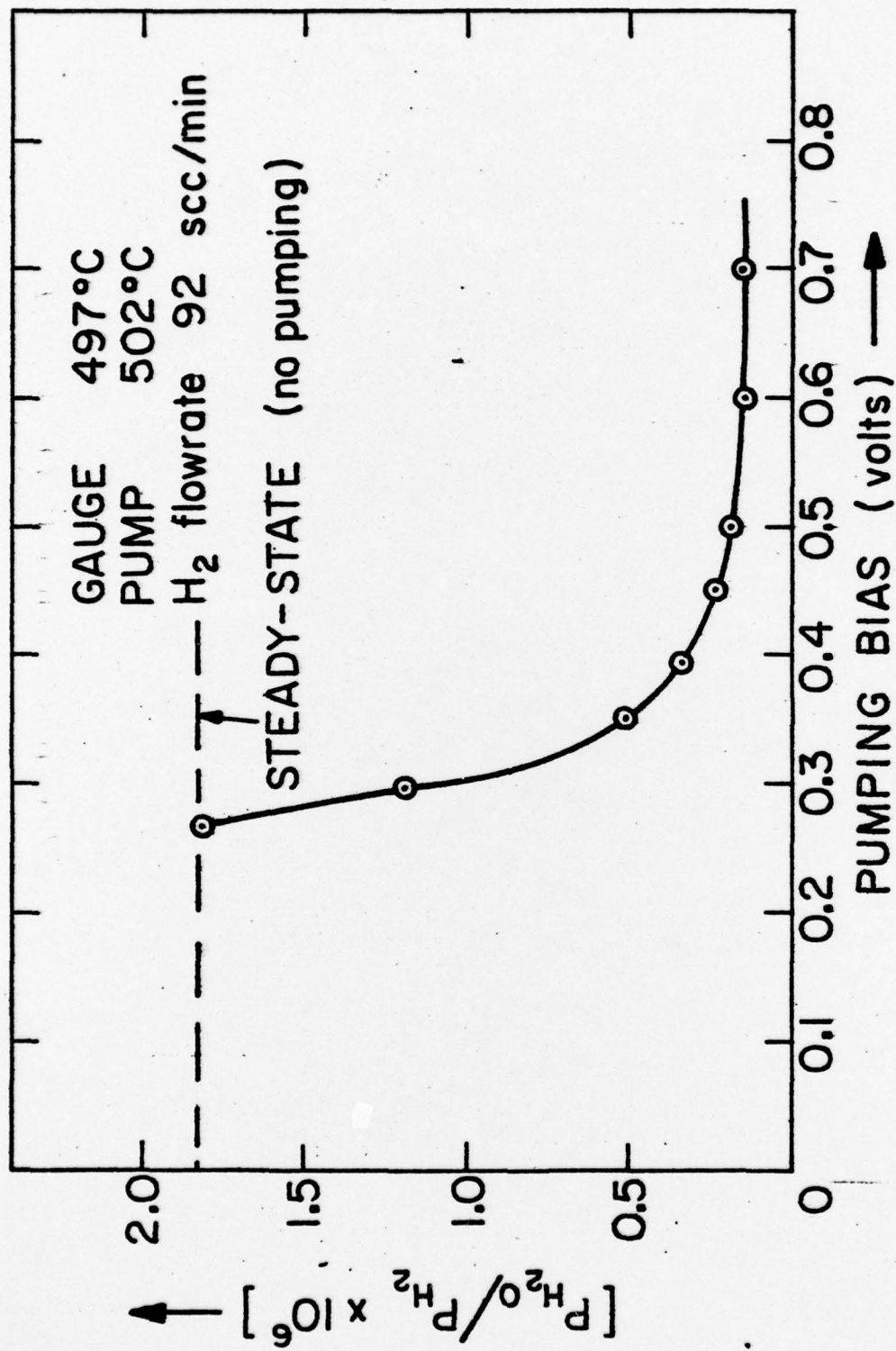
Fig. 4. Dependence of P_{H_2O}/P_{H_2} on Pump Bias

-16b-

sources: (1) it represents the residual H_2O not removed by the pump because of insufficient contact time, (2) it is due to outgassing and diffusion of oxygen species through the hot quartz enveloped of the pump and heater, (3) leaks at the Joints and out gassing of the connecting pyrex lines are responsible, and (4) the minimum detection level is 0.15 ppm H_2O for a H_2 flow rate of 92 scc/min. because of the small electronic conductivity of the CSZ. Estimates for the electronic conductivity vary drastically.[2] The observed 0.15 ppm of H_2O corresponds to that expected for the highest estimate for the electronic conductivity. Based on unpublished work currently in progress, our results support a "middle of the road" value within the range of reported (with some extrapolation) electronic conductivities. Using this estimate we would expect the minimum measurable water concentration to be 0.005 to 0.05 ppm in a H_2 stream flowing at a rate of 100 scc/min. The apparent experimental limit of 0.15 ppm in a H_2 stream flowing at a rate of 100 scc/min. is diffusion of O_2 through the quartz envelopes of the pump and gauge and its reaction with H_2. The observed minimum H_2O concentration dropped to 0.06 ppm for H_2 flow rates between 300 and 400 scc/min. as shown in Figure 5. This limit represents a combination of pump reaction times, gauge detection limit and diffusion/outgassing of the quartz envelopes. Indications of the latter are higher H_2O concentrations noted for given flow rates upon raising the temperature of the pump and its envelope.
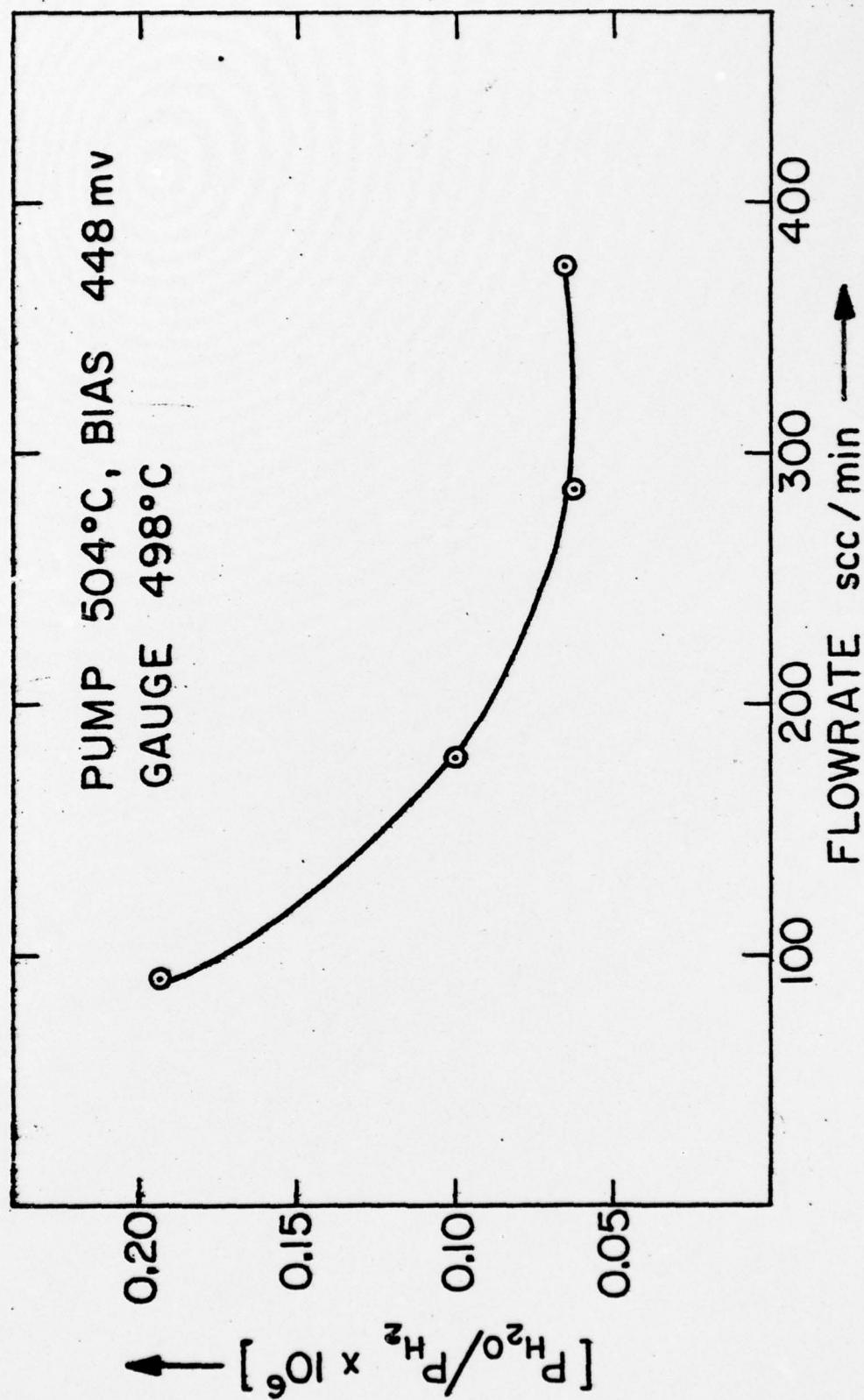
Fig. 5. Ratio of P_{H_2O} to P_{H_2} as a Function of H_2 Flow Rate

-17a-

EPITAXIAL REACTOR DESIGN

The initial epitaxial system consisted of a two port horizontal slider system made from Poco fine grained carbon and contained in a quartz envelope. This system could not be outgassed to the extent of reducing the water concentration below ~ 10 ppm. At that time the CSZ gauge design and reference gas supply were relatively crude. Fluctuations of a few ppm were suspect. This compares to observed variation of H_2O concentrations down to ~ 0.1 ppm as being the stability limits of the CSZ gauges.

GaAs films grown in this early system lacked the smooth finish needed for fractional micron growth and showed excessive signs of pre-growth etching of a type indicative of water vapor, i.e., there were no signs of free Ga drops such as one finds if the surface erodes by the simple loss of As. The inability to grow smooth GaAs films on GaAs precludes any chance of success for the growth of thin $Ga_xIn_{1-x}As$ and $GaAs_xSb_{1-x}$ films. One possibility is the presence of an oxide film on GaAs which is more difficult to reduce than Ga_2O_3.

The approach to test verify this point was based upon earlier observations directed towards measuring the solubility of oxygen in liquid Ga. It was noted that oxygen could be pumped out of Ga melts in contact with CSZ surfaces so that the dissolved oxygen activity was equivalent to H_2 atmospheres containing 0.025 ppm H_2O at 600° and 4×10^{-5} ppm at $500^\circ C$. This was so even through the H_2 atmospheres containing 6 and 0.6 ppm H_2O respectively. These large differences, resulting from the

relatively slow reaction rates of H_2O in H_2 with Ga to form dissolved oxygen, can be removed from Ga by electrolytic pumping of the CSZ. We attempted to electrolytically pump oxygen from the Ga melt into its surrounding H_2 atmosphere using an apparatus shown in Figure 6.

In this arrangement the electrolytic cell consists of the CSZ cylinder with a Pt electrode on its outside surface biased positively with respect to the Ga melt electrode contacting the inner CSZ surface and the carbon slider/guide parts. A Pt wire contacted these to complete the leads within the quartz envelope. The quality of GaAs epitaxial films grown without biasing of the melt pumps was not appreciable better than without. These observations and recent studies support the position that residual oxides on GaAs remaining from H_2O rinsing after aqueous etching are reducible in nominally pure H_2 atmospheres containing H_2O at concentrations of a "few" ppm.

We now believe the most adverse effect of H_2O in the H_2 stream is the selected etching it produces on the polished substrate surface. This etching is selective and tends to produce a faceted surface, one which is highly selective with respect to subsequent nucleation. The net result is that initial vapor etching of the substrates grossly complicates solution epitaxial growth of thin films.

Towards the goal of removing H_2O [or equivalently, $Ga_2O(g)$] in the epitaxial growth apparatus, the carbon parts were replaced with quartz. Features of this all quartz assembly are shown in Figure 7. A quartz plate could be used to cover the GaAs substrate, dummy substrate and
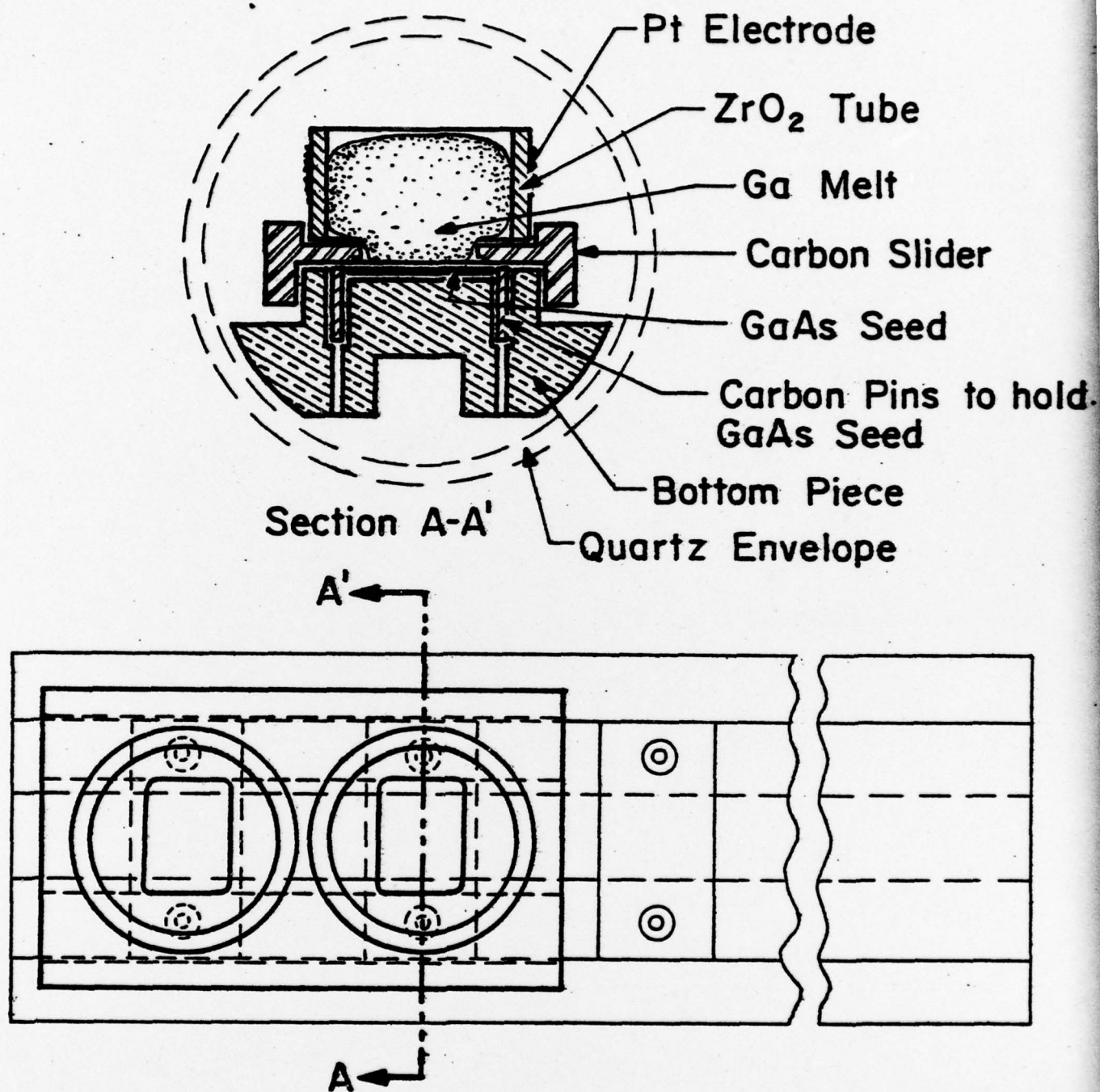
-19-

Fig. 6. Carbon/ZrO$_2$ Assembly for Liquid Phase Epitaxy with Provision for Electrolytic Pumping of Melts

Fig. 7. Quartz Assembly for Liquid Phase Epitaxy

source wafers, during the warm up/temperature equilibration. Cajon O-ring fittings were used for sealing the quartz guide tube and its push tube which located the melts relative to the substrate. Optimum H_2O concentrations in this sytem under various conditions are given below.

The following values are the lowest H_2O concentrations in the exit H_2 stream flowing at the rate of 15 scc/min. and at $700^{\circ}C$ under various conditions: a) envelope only, 1.2 ppm; b) slider assembly in the furnace but without GaAs or Ga, 3 ppm; and c) slider assembly in the furnace and loaded with Ga and GaAs, 4 ppm. At $800^{\circ}C$ the minimum H_2O content varied from 6 to 9 ppm. Following ~20 hrs. exposure of the CSZ gauge to the exhaust H_2 from the loaded system at $800^{\circ}C$ the gauge began to fail due to arsenic contamination of its Pt electrode. Traces of arsenic limits the Pt electrodes catlytic function of equilibrating the CSZ surface with the atmosphere. The failure mode of the gauge was to overestimate the H_2O content by ~1-2 orders of magnitude. It is useful to know that under extreme conditions of very low H_2O concentrations or electrode poisoning the gauges tend to err in the direction of over estimating the H_2O/H_2 ratios.

A further refinement was made in the system. The quartz cylinders comprising the vertical walls of the melt containers were replaced with sections of CSZ cylinders similar to those with the carbon slider assembly. Their effectiveness was not extensively tested because of time limitations. Preliminary results were not encouraging with respect to smoother thin epitaxial GaAs films. This result was not unexpected since we believe the basic limitation was the inability to limit the pre-growth vapor etching of the substrates.

SUMMARY OF GROWTH EXPERIMENTS

As noted earlier, our attempts to establish adequate growth conditions for GaAs films with thicknesses of 1 µm or less were unsuccessful. Substrate orientations of 311, 3$\bar{1}\bar{1}$, 211, 2$\bar{1}\bar{1}$, 100 and 111 were tried. Cooling rates varying from 0.1 to 2°C/min. with cooling intervals from 0.05 to 10°C were used. The general smoothness of the epitaxial films grown at 600°C was poorer than those at 700 and 800°C. We were unable to grow films in the thickness 1 µm range. This limitation is attributed to pregrowth vapor etching of the substrates by H_2O in the H_2. Failure with GaAs on GaAs precluded success with GaAs-GaSb and GaAs-InAs alloys.

Excess H_2O in the reactor gas stream also precluded full testing of attempts to get extremely high density nucleation by wetting the substrate surface with upwards of 10^8 Ga droplets/cm^2 prior to exposing the substrate to the melt. These droplets, made by reducing an anodic oxide with the H_2, also reacted with the residual H_2O during the temperature equilibration period.

Films of GaAs-InAs and GaAs-GaSb were supplied. These were of relatively poor quality--much poorer than we had previously grown in a vertical dipping system.

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1. C. T. Li, "Preparation and Properties of $Ga_{(1-x)}In_xAs$ and $GaAs_{(1-x)}Sb$ Alloys," Ph. D. Dissertation, University of Southern California, 1970.

2. T. H. Etsell and S. N. Flengas, Metallurgical Transactions $\underline{3}$, 27 (1972).